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Dichloridobis(picolinohydrazide)-cadmium(II)

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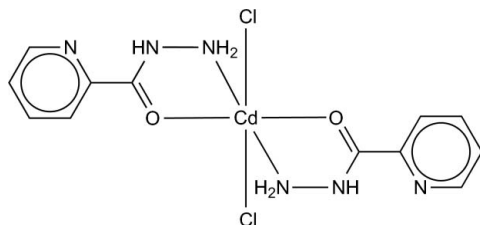
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}—\text{C}) = 0.004$ Å; R factor = 0.027; wR factor = 0.067; data-to-parameter ratio = 13.3.

The title compound, $[\text{CdCl}_2(\text{C}_6\text{H}_7\text{N}_3\text{O})_2]$, was obtained unintentionally as a product of an attempted reaction of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and picolinic acid hydrazide, in order to obtain a cadmium(II) complex analogous to a 15-metallacrown-5 complex of the formula $[\text{MCu}_5\text{L}_5]\text{X}_n$, with M = a central metal ion, L = picolinic acid hydrazide and $X = \text{Cl}^-$, but with cadmium the only metal present. The coordination geometry around the Cd^{II} atom can be considered as distorted octahedral, with two bidentate picolinic acid hydrazide ligands, each coordinating through their carbonyl O atom and amino N atom, and two chloride anions. In the crystal structure, intermolecular $\text{N}—\text{H} \cdots \text{Cl}$ and $\text{N}—\text{H} \cdots \text{N}$ hydrogen bonds link the molecules into a two-dimensional network parallel to the (100) plane. The pyridine rings of adjacent networks are involved in π – π stacking interactions, the minimum distance between the ring centroids being 3.693 (2) Å.

Related literature

For related literature, see: Allen (2002); Bodwin *et al.* (2001); Seda *et al.* (2007); Parac-Vogt *et al.* (2006); Stemmler, Kampf *et al.* (1996); Stemmler, Barwinski *et al.* (1996); Zareef *et al.* (2006); Tsintsadze *et al.* (1979); Klingele & Brooker (2004).



Experimental

Crystal data

$[\text{CdCl}_2(\text{C}_6\text{H}_7\text{N}_3\text{O})_2]$
 $M_r = 457.60$
 Monoclinic, $C2/c$
 $a = 16.9951$ (7) Å
 $b = 6.7365$ (2) Å
 $c = 14.3313$ (6) Å
 $\beta = 98.221$ (3)°

$V = 1623.89$ (11) Å³
 $Z = 4$
 Cu $K\alpha$ radiation
 $\mu = 13.97$ mm⁻¹
 $T = 293$ (2) K
 $0.30 \times 0.15 \times 0.10$ mm

Data collection

Bruker SMART 6000
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 1997)
 $T_{\min} = 0.116$, $T_{\max} = 0.247$

5326 measured reflections
 1395 independent reflections
 1349 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.067$
 $S = 1.11$
 1395 reflections

105 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.52$ e Å⁻³
 $\Delta\rho_{\min} = -0.90$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
$\text{N2}—\text{H2A} \cdots \text{Cl1}^{\text{i}}$	0.86	2.49	3.321 (3)	161
$\text{N3}—\text{H3A} \cdots \text{N1}^{\text{ii}}$	0.90	2.22	3.086 (4)	162
$\text{N3}—\text{H3B} \cdots \text{Cl1}^{\text{iii}}$	0.90	2.59	3.379 (2)	147

Symmetry codes: (i) $x, -y, z + \frac{1}{2}$; (ii) $-x, -y, -z + 1$; (iii) $-x, y - 1, -z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2521).

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supplementary materials

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Dichloridobis(picolinohydrazide)cadmium(II)

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Comment

Metallocrowns are cyclic polynuclear complexes, which are the inorganic analogues of crown ethers, both in structure and function (Bodwin *et al.*, 2001). In contrast to the numerous 12-metallacrown-4 structures reported, there are only a few examples of ligands capable of forming planar rings of the 15-metallacrown-5 structure type. Especially α -amino- and picolinehydroxamic acids have been used as precursor ligands in the synthesis of these complexes (Seda *et al.*, 2007; Parac-Vogt *et al.*, 2006; Stemmler, Kampf *et al.*, 1996; Stemmler, Barwinski *et al.*, 1996).

The title compound was obtained unintentionally as a product of an attempted reaction of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and picolinic acid hydrazide, in order to obtain a cadmium(II)-complex analogous to a 15-metallacrown-5, but with cadmium the only metal present. Here, picolinic acid hydrazide was used instead of various α -amino-, mandelo-, or picolinehydroxamic acids as a precursor ligand (Seda *et al.*, 2007; Parac-Vogt *et al.*, 2006; Stemmler, Kampf *et al.*, 1996; Stemmler, Barwinski *et al.*, 1996).

The asymmetric unit of the title compound consists of one-half molecule of the complex, with the Cd^{II} ion lying on a twofold rotation axis. The coordination geometry around the Cd^{II} ion can be considered as a slightly distorted octahedron, with two bidentate picolinic acid hydrazide ligands and two chloride anions (Fig. 1).

As observed in the structure of picolinic acid hydrazide (Zareef *et al.*, 2006), the aromatic C—C bond lengths within the phenyl ring vary between 1.375 (5) Å and 1.388 (5) Å. Additionally, an opening of the angles N1—C1—C2 (124.0 (3)°) and N1—C5—C4 (123.0 (3)°) is observed, due to the presence of the nitrogen atom, N1 (Zareef *et al.*, 2006). As a consequence, a decrease of the ring angles C1—C2—C3 (117.8 (3)°), C2—C3—C4 (119.6 (3)°), C3—C4—C5 (118.5 (3)°) and C1—N1—C5 (117.1 (3)°) is noticed. The pyridine ring is twisted away with respect to the rest of the picolinic acid hydrazide molecule; the dihedral angle between the N1/C1—C5 and C1/C6/O1/N2/N3 is 23.3 (1)°.

In the crystal structure, intermolecular N—H \cdots Cl and N—H \cdots N hydrogen bonds link the molecules in to a two-dimensional network parallel to the (1 0 0) plane (Fig. 2). In addition, π - π stacking interactions are observed between the pyridine rings of the adjacent networks, with the distance between the ring centroids being 3.815 (2) or 3.693 (2) Å.

The reported structure is homologous to the structure of dichloro-bis(picolinic acid hydrazide)-manganese (Tsintsadze *et al.*, 1979) (reference code PHYZMN, CSD (Version 5.28) (Allen, 2002)).

Experimental

The ligand picolinic acid hydrazide was prepared as described previously (Klingele & Brooker, 2004), by refluxing the respective picolinic acid ethylester for 4 h with a slight excess of hydrazine monohydrate. The product was recrystallized from ethanol. The cadmium complex was synthesized by adding a solution of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.229 g, 1 mmol) in methanol (20 ml) to a stirred solution of picolinic acid hydrazide (0.274 g, 2 mmol) in methanol (20 ml). The mixture was stirred for

1 h at room temperature. Colourless crystals were obtained after leaving the solution to evaporate for 3 d. The crystals were collected by filtration, washed with cold methanol and dried in a desiccator.

Refinement

All H atoms were initially located in a difference Fourier map and later placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å, N—H = 0.86 or 0.90 Å and $U_{\text{iso}}(\text{H}) = 1.2_{\text{eq}}(\text{C})$.

Figures

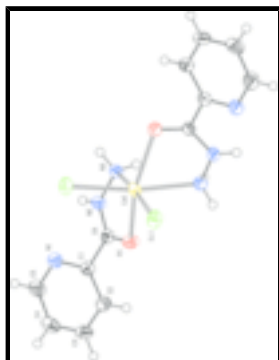


Fig. 1. Coordination geometry of the title compound, showing the atom-labelling scheme of the asymmetric unit and 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by the symmetry operation $(-x, y, 1/2 - z)$.

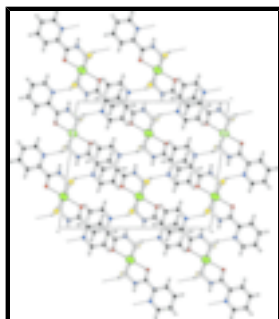


Fig. 2. Crystal packing of the title compound, viewed along the b axis. Hydrogen bonds are shown as dashed lines.

Dichloridobis(picolinohydrazide)cadmium(II)

Crystal data

$[\text{CdCl}_2(\text{C}_6\text{H}_7\text{N}_3\text{O})_2]$

$M_r = 457.60$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 16.9951\ (7)\ \text{\AA}$

$b = 6.7365\ (2)\ \text{\AA}$

$c = 14.3313\ (6)\ \text{\AA}$

$\beta = 98.221\ (3)^\circ$

$V = 1623.89\ (11)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 904$

$D_x = 1.872\ \text{Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54178\ \text{\AA}$

Cell parameters from 2348 reflections

$\theta = 5.3\text{--}71.6^\circ$

$\mu = 13.97\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Rod, colourless

$0.30 \times 0.15 \times 0.10\ \text{mm}$

Data collection

Bruker SMART 6000 diffractometer	1395 independent reflections
Radiation source: fine-focus sealed tube	1349 reflections with $I > 2\sigma(I)$
Monochromator: crossed Göbel mirrors	$R_{\text{int}} = 0.036$
$T = 293(2)$ K	$\theta_{\text{max}} = 66.6^\circ$
ω and ϕ scans	$\theta_{\text{min}} = 5.3^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$h = -20 \rightarrow 17$
$T_{\text{min}} = 0.116$, $T_{\text{max}} = 0.247$	$k = -8 \rightarrow 7$
5326 measured reflections	$l = -16 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.027$	H-atom parameters constrained
$wR(F^2) = 0.067$	$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 1.6198P]$
$S = 1.11$	where $P = (F_o^2 + 2F_c^2)/3$
1395 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
105 parameters	$\Delta\rho_{\text{max}} = 0.52 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.90 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.18958 (16)	-0.0129 (4)	0.4884 (2)	0.0251 (6)
C2	0.26626 (17)	0.0003 (4)	0.4662 (2)	0.0285 (6)
H2	0.2758	-0.0039	0.4039	0.034*
C3	0.32779 (17)	0.0197 (4)	0.5395 (2)	0.0325 (7)
H3	0.3799	0.0312	0.5272	0.039*

supplementary materials

C4	0.31165 (19)	0.0218 (5)	0.6308 (3)	0.0375 (7)
H4	0.3525	0.0319	0.6812	0.045*
C5	0.2330 (2)	0.0087 (5)	0.6461 (2)	0.0392 (8)
H5	0.2222	0.0111	0.7079	0.047*
C6	0.12048 (16)	−0.0340 (4)	0.4117 (2)	0.0227 (5)
N1	0.17201 (15)	−0.0072 (4)	0.57595 (18)	0.0313 (6)
N2	0.05532 (15)	−0.1154 (3)	0.43715 (19)	0.0253 (5)
H2A	0.0547	−0.1535	0.4943	0.030*
N3	−0.01277 (14)	−0.1381 (3)	0.36872 (18)	0.0239 (5)
H3A	−0.0574	−0.1181	0.3945	0.029*
H3B	−0.0144	−0.2608	0.3436	0.029*
O1	0.12502 (12)	0.0236 (3)	0.33022 (15)	0.0307 (5)
Cl1	0.03593 (5)	0.36372 (10)	0.13274 (6)	0.03299 (19)
Cd1	0.0000	0.10888 (4)	0.2500	0.02458 (13)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0255 (15)	0.0245 (13)	0.0247 (16)	0.0018 (10)	0.0019 (11)	0.0020 (10)
C2	0.0266 (15)	0.0279 (13)	0.0309 (17)	0.0035 (10)	0.0040 (12)	0.0014 (11)
C3	0.0203 (14)	0.0309 (15)	0.045 (2)	0.0009 (11)	0.0011 (12)	0.0001 (13)
C4	0.0320 (17)	0.0385 (17)	0.038 (2)	−0.0031 (13)	−0.0099 (13)	0.0008 (13)
C5	0.0374 (18)	0.053 (2)	0.0251 (19)	−0.0067 (14)	−0.0012 (13)	0.0007 (14)
C6	0.0240 (13)	0.0237 (13)	0.0202 (15)	0.0035 (10)	0.0029 (10)	0.0017 (10)
N1	0.0280 (13)	0.0412 (14)	0.0237 (15)	−0.0035 (10)	0.0006 (10)	0.0008 (10)
N2	0.0239 (12)	0.0305 (13)	0.0207 (15)	−0.0016 (8)	0.0006 (10)	0.0032 (8)
N3	0.0220 (12)	0.0272 (11)	0.0216 (14)	−0.0028 (9)	0.0002 (9)	−0.0009 (9)
O1	0.0239 (10)	0.0433 (12)	0.0245 (12)	−0.0003 (8)	0.0018 (8)	0.0058 (9)
Cl1	0.0444 (4)	0.0284 (3)	0.0278 (5)	0.0019 (3)	0.0107 (3)	0.0038 (3)
Cd1	0.02608 (18)	0.02668 (18)	0.0197 (2)	0.000	−0.00130 (11)	0.000

Geometric parameters (\AA , $^\circ$)

C1—N1	1.331 (4)	C6—N2	1.332 (4)
C1—C2	1.388 (4)	N2—N3	1.414 (3)
C1—C6	1.497 (4)	N2—H2A	0.86
C2—C3	1.378 (4)	N3—Cd1	2.412 (2)
C2—H2	0.93	N3—H3A	0.90
C3—C4	1.375 (5)	N3—H3B	0.90
C3—H3	0.93	O1—Cd1	2.338 (2)
C4—C5	1.387 (5)	Cl1—Cd1	2.5372 (7)
C4—H4	0.93	Cd1—O1 ⁱ	2.338 (2)
C5—N1	1.342 (4)	Cd1—N3 ⁱ	2.412 (2)
C5—H5	0.93	Cd1—Cl1 ⁱ	2.5371 (7)
C6—O1	1.243 (4)		
N1—C1—C2	124.0 (3)	N2—N3—Cd1	105.50 (15)
N1—C1—C6	115.9 (2)	N2—N3—H3A	110.6
C2—C1—C6	120.1 (3)	Cd1—N3—H3A	110.6

C3—C2—C1	117.8 (3)	N2—N3—H3B	110.6
C3—C2—H2	121.1	Cd1—N3—H3B	110.6
C1—C2—H2	121.1	H3A—N3—H3B	108.8
C4—C3—C2	119.6 (3)	C6—O1—Cd1	111.37 (17)
C4—C3—H3	120.2	O1—Cd1—O1 ⁱ	151.56 (11)
C2—C3—H3	120.2	O1—Cd1—N3	69.56 (8)
C3—C4—C5	118.5 (3)	O1 ⁱ —Cd1—N3	90.59 (8)
C3—C4—H4	120.7	O1—Cd1—N3 ⁱ	90.59 (8)
C5—C4—H4	120.7	O1 ⁱ —Cd1—N3 ⁱ	69.56 (8)
N1—C5—C4	123.0 (3)	N3—Cd1—N3 ⁱ	92.74 (12)
N1—C5—H5	118.5	O1—Cd1—Cl1 ⁱ	97.38 (6)
C4—C5—H5	118.5	O1 ⁱ —Cd1—Cl1 ⁱ	101.77 (5)
O1—C6—N2	123.4 (3)	N3—Cd1—Cl1 ⁱ	86.86 (6)
O1—C6—C1	120.9 (2)	N3 ⁱ —Cd1—Cl1 ⁱ	171.32 (6)
N2—C6—C1	115.7 (2)	O1—Cd1—Cl1	101.77 (5)
C1—N1—C5	117.1 (3)	O1 ⁱ —Cd1—Cl1	97.38 (6)
C6—N2—N3	119.0 (2)	N3—Cd1—Cl1	171.32 (6)
C6—N2—H2A	120.5	N3 ⁱ —Cd1—Cl1	86.86 (6)
N3—N2—H2A	120.5	Cl1 ⁱ —Cd1—Cl1	94.84 (3)
N1—C1—C2—C3	0.3 (4)	C1—C6—N2—N3	179.3 (2)
C6—C1—C2—C3	179.9 (3)	C6—N2—N3—Cd1	-24.3 (3)
C1—C2—C3—C4	1.1 (4)	N2—C6—O1—Cd1	26.2 (3)
C2—C3—C4—C5	-1.4 (5)	C1—C6—O1—Cd1	-153.2 (2)
C3—C4—C5—N1	0.4 (5)	C6—O1—Cd1—O1 ⁱ	-75.72 (18)
N1—C1—C6—O1	155.8 (3)	C6—O1—Cd1—N3	-27.42 (18)
C2—C1—C6—O1	-23.9 (4)	C6—O1—Cd1—N3 ⁱ	-120.12 (19)
N1—C1—C6—N2	-23.6 (4)	C6—O1—Cd1—Cl1 ⁱ	56.43 (19)
C2—C1—C6—N2	156.7 (3)	C6—O1—Cd1—Cl1	152.96 (18)
C2—C1—N1—C5	-1.2 (4)	N2—N3—Cd1—O1	25.21 (15)
C6—C1—N1—C5	179.1 (3)	N2—N3—Cd1—O1 ⁱ	-175.62 (16)
C4—C5—N1—C1	0.9 (5)	N2—N3—Cd1—N3 ⁱ	114.82 (18)
O1—C6—N2—N3	-0.1 (4)	N2—N3—Cd1—Cl1 ⁱ	-73.86 (16)

Symmetry codes: (i) $-x, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots Cl1 ⁱⁱ	0.86	2.49	3.321 (3)	161
N3—H3A \cdots N1 ⁱⁱⁱ	0.90	2.22	3.086 (4)	162
N3—H3B \cdots Cl1 ^{iv}	0.90	2.59	3.379 (2)	147

Symmetry codes: (ii) $x, -y, z+1/2$; (iii) $-x, -y, -z+1$; (iv) $-x, y-1, -z+1/2$.

Fig. 1

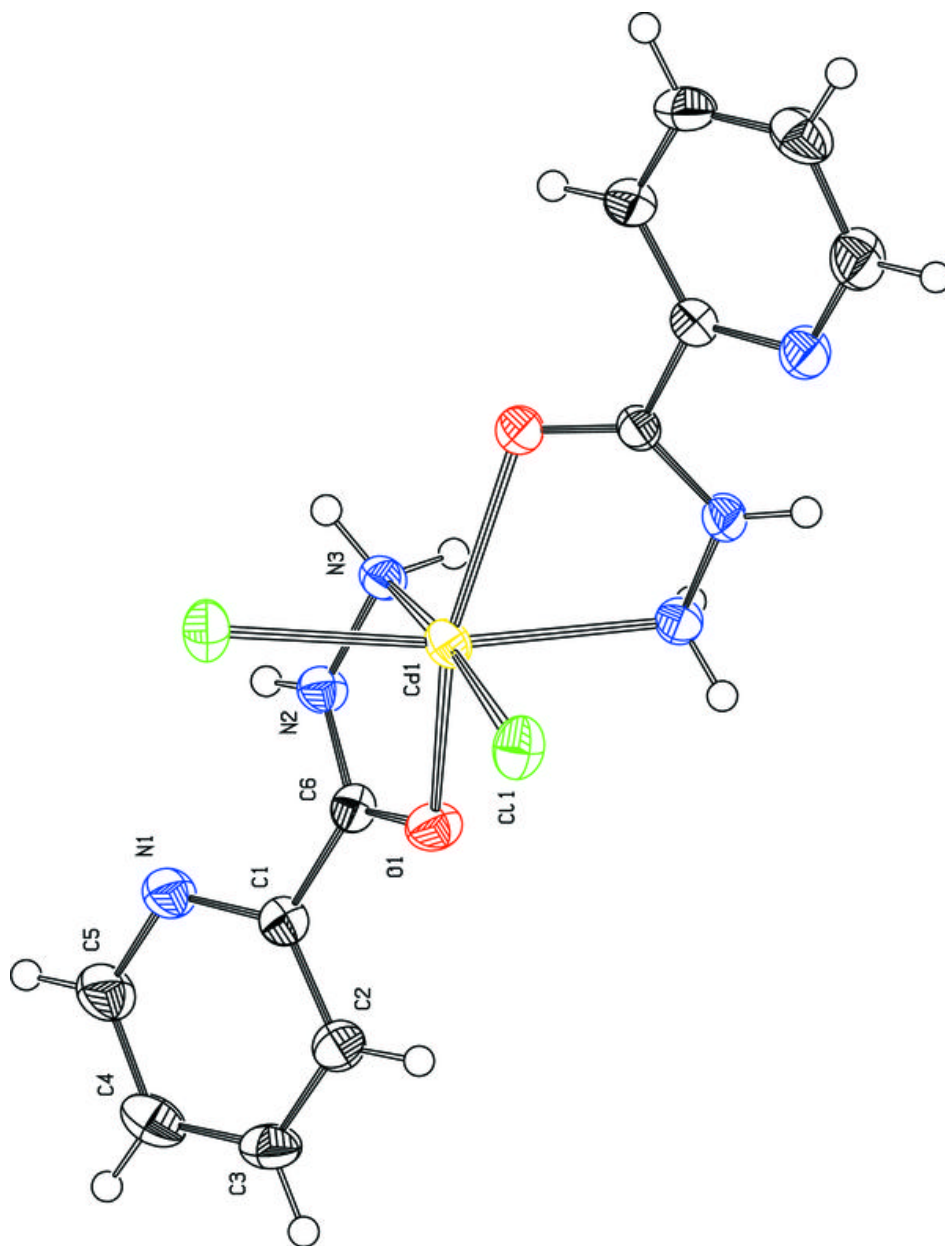


Fig. 2

